

PATENT SPECIFICATION

NO DRAWINGS

936.770

936.770



Date of Application and filing Complete Specification: Sept. 29, 1961.

No. 35084/61.

Application made in United States of America (No. 64273) on Oct. 24, 1960.

Complete Specification Published: Sept. 11, 1963.

© Crown Copyright 1963.

Index at acceptance:—Class 2(6), P10C(6A:6B:8A:8B:12B:12X:14B:16B:16C:18:20B:20C), P10D(1A:1X:2A:2X), P10K10.

International Classification:—C08f.

COMPLETE SPECIFICATION

Improvements relating to Halogen-Containing Hydrocarbon Polymers

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the stabilization of polymeric halogen-containing hydrocarbons.

The invention will be described primarily as it applies to polyvinyl chloride or copolymers of vinyl chloride having vinyl chloride as the major constituent, and their formation into films for use in packaging applications. However, it is applicable also to homopolymers and copolymers of vinyl fluoride and indeed to all polymeric materials whose thermal decomposition, leading to discoloration, is at least partially attributable to the loss of halogen acid. Moreover it includes generally the shaping of all the above polymeric materials, especially but not exclusively, into films, filaments, fibres, foils and coatings. Examples of polymers other than those of vinyl chloride and vinyl fluoride to which the invention can be applied include vinylidene chloride polymers, vinylidene chloride-vinyl chloride copolymers, vinylidene fluoride polymers.

The invention consists in compositions composed primarily of a halogen-containing hydrocarbon polymer with smaller amounts of at least one olefinically unsaturated terpene or an oxygen, hydrocarbon or halogen derivative of an olefinically unsaturated terpene and of at least one Thio compound having the formula $R-S-H$ or $R-S-S-R^1$ wherein R and R^1 are the same or different and are alkyl, hydroxyalkyl, thioalkyl, carboalkoxyalkyl, carboxyalkyl, aralkyl, aryl, alkaryl, haloaryl, thioaryl, thioalkaryl, carboalkoxy- (Price 4s. 6d.)

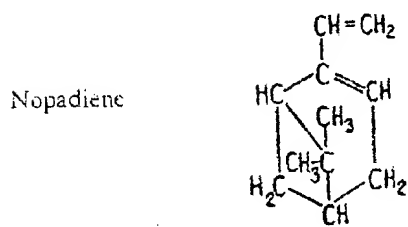
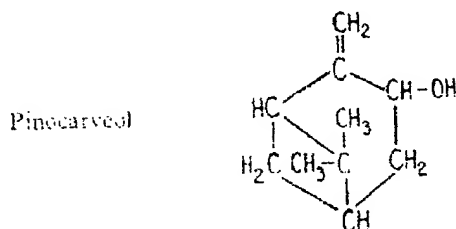
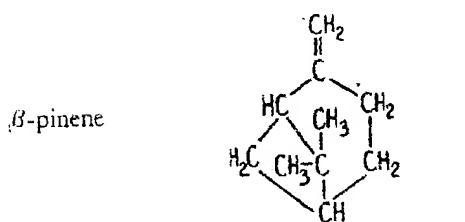
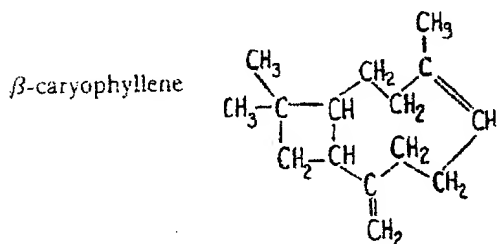
aryl, carboxyaryl, cycloalkyl, or thienyl groups, and also containing a small amount of a finely dispersed (as hereinafter defined) organometallic compound of zinc having the formula R^2_2Zn wherein R^2 is an aryl group or an alkyl group having 1—18 carbon atoms or of a finely dispersed zinc derivative of a compound having at least one active hydrogen atom [as detected by the Zerewitinoff Test (described by Zerewitinoff in Berichte, 40, 2023 (1907), and 41, 2233 (1908) and by Kohler in Journal American Chemical Society, 49, 3181 (1927))] and an ionization constant of at least 1×10^{-16} . (The operability of a zinc derivative can be determined by substituting hydrogen for zinc in the derivative and noting whether the resulting compound has at least one active hydrogen and a minimum ionization constant of 1×10^{-16}).

The preferred halogen-containing hydrocarbon polymers are those in which the halogen is fluorine or chlorine. These include polyvinyl chloride, polyvinyl fluoride, polyvinylidene chloride, polyvinylidene fluoride and vinyl chloride-vinylidene chloride copolymers.

The term "olefinically unsaturated terpenes" includes both the naturally-occurring and synthetically-prepared olefinically unsaturated terpenes and terpene mixtures. These have the general formula $(C_5H_8)_x$, wherein x is 2 to 6, and may be monocyclic, bicyclic, tricyclic or polycyclic. The preferred terpene compounds are olefinically unsaturated bicyclic terpenes and their oxygen, hydrocarbon and halogen derivatives, wherein one ring of the bicyclic terpene contains no more than four carbon atoms. Even more preferred are those terpene compounds which fulfil the above requirements and in which also the second ring carries at least one exo-alkylene group.

β -caryophyllene, β -pinene, pinocarveol (a terpene alcohol), and nopadiene (a terpene hydrocarbon), which are the outstanding com-

- pounds for use in the invention, in addition to having an exo double bond (an exo-alkylene group), are bicyclic, with one four membered ring. The first three of these are further distinguished by having the exo double bond attached directly to the larger ring structure of the compound. The distinguishing characteristics common to these compounds will be clearly apparent from their structural formulae:



- Other terpene compounds useful in the present invention include pinocarvone, sabinene, sabinol, α -thujene, β -thujene, α -pinene, umbellulone, Δ^3 -carene, Δ^4 -carene, myrtenol, myrtenal, verbenone, α -fenchene, β -fenchene, camphene, santene, bornylene, apobornylene, cadinene, selinene, di-pentene (d,l-limonene), β -terpineol, α -terpineol, carvone, menthene, bis-abolene, zingiberene, pinocarvyl chloride, myrcene, geraniol, d,l-nerolidol, linalool, citronellal, alloocimene, and citral.

- Of the sulphur-containing (thio) organic compounds of formula $R-S-S-R^1$ or $R-S-H$, the preferred compounds are the organic thiols, $R-S-H$, wherein R is an

alkyl group containing at least 8 carbon atoms, such as decanethiol, dodecanethiol and octadecanethiol. In addition to these thiols and those used in the Examples, thiols which are operable in this invention include: 1-hexanethiol, 2-hexanethiol, 2-dodecanethiol, ethane-1,2-dithiol, propane-1,3-dithiol, dodecane-1,10-dithiol, 1,4-dimercaptomethylbenzene, 1,4-dimercaptomethyl-2,3,5,6-tetramethylbenzene, β -phenylethylthiol, triphenylmethanethiol, α -mercaptoacetic acid, β -mercaptopropionic acid, butyl γ -mercaptopropionate, butyl α -mercaptobutyrate, butyl β -mercaptobutyrate, butyl γ -mercaptobutyrate, butyl α -mercapto-phenylacetate, 2-thioethanol, thioglycerol, naphthalene-2-thiol, benzenethiol, *o*-, *m*- and *p*-thiocresols, 4-*t*-butylthiophenol, 4-chlorobenzenethiol, 4-alkoxybenzenethiol, furfurylthiol, *o*-mercaptobenzoic acid, butyl *m*-mercaptobenzoate, butyl *p*-mercaptobenzoate and butyl 4-mercaptophenyl acetate.

Disulphides which may be used may be prepared by the procedure described by Ritter and Sharp, Journal of the American Chemical Society, 59, 2351 (1937). Specifically, a solution of a thiol in an equal volume of glacial acetic acid is introduced into a flask fitted with stirrer, dropping funnel and thermometer. The solution is cooled to 5° C. and, thereafter, a solution of hydrogen peroxide (25%—30%) in an equal volume of glacial acetic acid is added dropwise. The rates of addition and cooling are adjusted to keep the temperature of the reaction mixture below 20° C. The addition of the oxidizing solution is continued until a test with starch-iodide paper indicates that the peroxide is no longer being consumed. The reaction mixture is slowly warmed to room temperature (25—30° C.) and the upper (disulphide) layer which separates is removed, washed first with 20% potassium hydroxide solution and then with water, and dried over anhydrous potassium carbonate prior to use.

Among the useful disulphides are: bis-dodecane disulphide, the disulphide of isooctyl β -mercaptopropionate, bis-*t*-butylphenyl disulphide, bis- β -phenylethane disulphide, bis-*t*-hexadecane disulphide, bis-2-hydroxyethane disulphide, bis-2-mercaptoethane disulphide, bis-phenyl disulphide, bis-4-chlorobenzene disulphide, bis-2-mercapto-4-methylbenzene disulphide, bis-4-mercaptomethylbenzene disulphide, the disulphide of butyl α -mercapto-phenyl acetate, the disulphide of 2-mercaptobenzoic acid, bis-cyclohexane disulphide, bis-2-thiophene disulphide, decane-octadecane disulphide, decane glyceryl disulphide, the mixed disulphide from 1,10-decanedithiol and isooctyl β -mercaptopropionate, the mixed disulphide from benzylthiol and thiophenol, the mixed disulphide from 4-chlorobenzenethiol and 4-mercaptomethylbenzenethiol, the mixed disulphide from butyl α -mercaptophenyl

acetate and 2-mercaptobenzoic acid, and the mixed disulphide from cyclohexanethiol and 2-thiophenethiol.

The amount of terpene or terpene derivative and sulphur-containing organic compound used, particularly in polyvinyl chloride compositions to be melt-extruded into films, should be enough to provide adequate thermal stability during the forming operation but not enough to affect the properties of the resulting film adversely. Concentrations of at least 1% of each of these ingredients, i.e., of the terpene or terpene derivative and the thio compound, based on the weight of the additives plus polymer, have been found most useful. The maximum amounts to be used will depend on the process of forming the shaped structures, subject to the maximum concentration of these additives in the ultimate product being preferably no greater than a total of 15%. This means that for melt-extrusion or dispersion-coalescence processes, 2—15%, may be used in the starting mixture. In solvent casting, where the additives may be evaporated during formation of the shaped structure, a much higher concentration may be used in the starting composition. In the preferred systems, percentages of 4—10% have been found most useful, the ratio of the thiol to the terpene in the stabilizer being from 0.2 to 2.

The compounds of zinc that are most useful in this invention are the carboxylic acid salts, the mercaptides, the hydroxide, the alkoxides, the aryloxides and the organometallic compounds of zinc, i.e., compounds having the

formula R^{11}_2Zn , $(R^{11}-\overset{\overset{O}{\parallel}}{C}-O)_2Zn$, $R^{11}_2S_2Zn$ and $Zn(OR^{11})_2$, wherein R^{11} is an aryl group or an alkyl group having 1—18 carbon atoms, and R^{11} is one of these or hydrogen.

The carboxylic acid salts include zinc laurate, zinc stearate, zinc 2-ethylhexoate, zinc palmitate, zinc oleate, zinc valerate, zinc caproate, zinc caprylate, zinc caprate, zinc myristate, zinc succinate, zinc adipate, zinc sebacate, zinc toluate and zinc terephthalate.

The zinc mercaptides include those of 1-dodecanethiol, isooctyl β -mercapto- β -proprionate, di-n-butyl thiomalate, cyclohexanethiol, t-butylthiophenol, thioglycerol, benzylthiol, thiophenol, 4-chlorobenzenethiol, toluene-3,4-dithiol, 4-mercaptomethylbenzenethiol, butyl α -mercaptophenyl acetate, 2-mercaptobenzoic acid, and 2-thiophenethiol.

The organo-zinc compounds having the formula R^{11}_2Zn , wherein there is a direct union of carbon with zinc, include dilauryl-zinc, dipropylzinc, diethylzinc, dihexylzinc, didecylzinc, dihexadecylzinc, dioctadecylzinc, diphenylzinc, ditolylzinc, dinaphthylzinc and dicyclohexylzinc.

The compounds of the formula $Zn(OR^{11})_2$

include zinc hydroxide, dilauryloxyzinc, dioctyloxyzinc, dicyclohexyloxyzinc, zinc acetyl acetate, the zinc alkoxide of triethyl citrate, alkoxo salts of zinc such as aluminium zinc isopropylate and potassium zinc methylate, diphenoxylzinc, dinaphthoxylzinc and ditoloxylzinc.

Other zinc compounds, while not preferred, which may be used include the salts of sulphonic and sulphinic acids, e.g., zinc ethyl sulphonate, zinc *p*-toluene sulphonate, zinc ethyl sulphinate, zinc benzene sulphonate; the sulphates, e.g., zinc sulphate, zinc lauryl sulphate, zinc phenyl sulphate; the sulphites, e.g., zinc sulphite; the halides, e.g., zinc chloride, zinc bromide; the phosphates, e.g., zinc phosphate; the silicates, e.g., zinc silicate; and the titanates, e.g., zinc titanate. The most preferred of the zinc compounds are zinc laurate, the zinc mercaptides of 1-dodecanethiol and isooctyl - β - mercapto-propionate, and dilauryl-zinc.

The amount of the zinc compound needed to achieve the results of the present invention is quite small. It has been found that the compound may be used in such quantities that the ultimate composition contains 3 to 50 parts by weight of zinc per million parts by weight of the polymer. More than 50 parts of zinc per million parts of polymer tends to degrade the polymer with accompanying discoloration. It is desirable to maintain the zinc compound in very fine form. Thus, the zinc compound should preferably be uniformly dispersed throughout the blend as particles having their greatest dimension not exceeding 1 micron. In this regard, it is possible to use metallic zinc and zinc oxide if they can be obtained as very fine particles and uniformly dispersed in the blend.

The surprisingly high degree of thermal stabilization obtained in the compositions of this invention permits forming them into shaped structures by processes in which they are held at elevated temperatures continuously for relatively long periods of time without encountering objectionable decomposition or discoloration. The compositions are thus uniquely suitable for commercially advantageous high speed, high temperature forming operations such as melt extrusion.

There are several advantages of the synergistic combinations of the terpenes, the sulphur-containing compounds and the zinc compounds over the use of any one class of these compounds alone. Thus, the combinations provide an extraordinarily high degree of stabilization and their use has substantially eliminated colour formation during extended extrusion operations involving polyvinyl chloride and similar halogenated hydrocarbon polymers. Since the sulphur-containing compounds and the zinc compounds in the quantities used are essentially non-toxic, the non-

toxicity of the terpenes is preserved in the combination. This is highly desirable in a composition used to prepare food packaging films.

- 5 The process for forming shaped structures in accordance with the invention involves blending a mixture of the halogen-containing hydrocarbon polymer, one of the aforementioned olefinically unsaturated terpenes or derivatives or terpenes, one of the aforementioned sulphur-containing organic compounds, and a specified compound of zinc, heating the mixture until it is converted into a homogeneous single phase composition, and thereafter forming the homogeneous single phase into a shaped structure and cooling the structure. Other additives may be used in the original blend such, for example, as fillers, dyes, special plasticizers, pigments and de-lusterants, as long as they do not tend to de- grade the polymer or detract from the bene- ficial effect of the essential additives.

- 25 The invention is illustrated but not limited by the following Examples, in which all parts are by weight unless otherwise specified.

EXAMPLE 1.

- A mixture of 90 parts of polyvinyl chloride resin (Dow 111-4 ("Dow" is a Registered Trade Mark) manufactured by the Dow Chemical Company), 5 parts of β -pinene, 5 parts of dodecanethiol and 10 parts per million of zinc as the mercaptide of dodecanethiol was prepared by mixing the components in a barrel tumbler for 3 hours. The mixture was extruded at a temperature of 195° C. through a conventional one-inch diameter extruder equipped with a 6 inch flat die and with a 7-mil lip opening and operating with a 50-100 mesh screen pack. Extrusion was continued for a period of 4 hours, by which time the film was clear, and completely free of colour and of bubbles.

In a control experiment, the same mixture was extruded with the exception that the zinc mercaptide of dodecanethiol was omitted. At the end of a four-hour extruder run the film obtained was clear and free of bubbles, but it had a yellow cast through the entire extrusion.

In another control experiment, a mixture of 98 parts of the same polyvinyl chloride resin and 2 parts of "Lubricin" V-3 (which consists principally of glyceryl triricinoleate and is manufactured by the Baker Castor Oil Company) was fed into the extruder again heated to 195° C. The mixture was converted to a bubbly, black mass part way through the heated zone to the extruder and could not be extruded owing to the plugging of the equipment.

EXAMPLES 2 AND 3.

These Examples were carried out to determine the effect on colour stability of various amounts of the zinc compound incorporated in the polyvinyl chloride composition under conditions simulating an actual extrusion.

Retention time of a polymeric composition in an extruder during forming is usually about 5 minutes. Therefore, it is critical that the polymer be stable for at least 5 minutes at the temperature in the extruder.

The time until onset of colour was determined by pressing in a Carver (Registered Trade Mark) press at 208° C. and 30 tons pressure (platen size—10 inches \times 14 inches) a mixture of 90 parts of polyvinyl chloride resin (Dow 111-4), 5 parts of β -pinene, 5 parts of isooctyl β -mercaptopropionate and from 0 to 500 parts of zinc as the mercaptide of isooctyl-mercaptopropionate per million parts of polyvinyl chloride. The mixture had been prepared as described in Example 1. The results are shown in Table I.

TABLE I

| Example | Zinc (ppm) | Time of onset of Colour (Minutes) |
|-----------|------------|-----------------------------------|
| Control A | 0 | 1—2 |
| 2 | 5 | 6 |
| 3 | 10 | 10 |
| Control B | 500 | 3 |

EXAMPLES 4—25.

- 85 Following the procedure described in Example 2, a number of stabilizer combinations were evaluated for their colour stabilizing

effect on polyvinyl chloride. The terpene used was 5% β -pinene. The sulphur-containing organic compound and the zinc compound were varied as shown in Table II.

TABLE II

| Example | % Sulphur Compound | Zinc Compound | Parts/ Million as Zinc | Time of Onset of Colour (Minutes) |
|---------|---|---|------------------------------|--|
| 4 | 5% t-butyl-thiophenol | mercaptide of t-butyl-thiophenol | 30 | 10 |
| 5 | " " " | " " " | 50 | 6 |
| 6 | 5% dodecanethiol | dodecanethiol** | 5 | 5 |
| 7 | " " | " | 20 | 10 |
| 6-7A* | " " | " | 100 | 2 |
| 6-7B* | None*** | " | 40 | 3 |
| 6-7C* | None*** | " | 100 | 2 |
| 8 | 5% dodecanethiol | isooctyl β -mercapto-propionate** | 20 | 11 |
| 9 | 5% benzylthiol | cyclohexanethiol** | 20 | 9 |
| 10 | 5% bis-dodecane disulphide | dodecanethiol** | 20 | 9 |
| 11 | 5% bis-t-hexadecane disulphide | t-hexadecanethiol** | 20 | 8 |
| 12 | 5% isooctyl β -mercaptopropionate | zinc laurate | 5 | 5 |
| 13 | " " " | " " | 20 | 10 |
| 12-13A* | " " " | " " | 60 | 3 |
| 14 | 5% dodecanethiol | dilauryloxyzinc | 5 | 6 |
| 15 | " " | " | 15 | 8 |
| 16 | " " | " | 20 | 10 |
| 17 | " " | zinc acetylacetonate | 5 | 6 |
| 18 | " " | " " | 15 | 8 |
| 19 | " " | " " | 30 | 10 |
| 20 | " " | zinc alkoxide of triethyl citrate | 7 | 6 |
| 21 | " " | " " | 15 | 7 |

* Controls that do not fall within invention.

** Zinc mercaptides of these compounds.

*** No terpene nor sulphur compound was used.

TABLE II (Cont.)

| Example | % Sulphur Compound | Zinc Compound | Parts/ Million as Zinc | Time of Onset of Colour (Minutes) |
|---------|--------------------|------------------------------|------------------------------|--|
| 22 | 5% dodecanethiol | potassium zinc methyllate | 5 | 6 |
| 23 | " " | " " | 15 | 10 |
| 24 | " " | diphenoxyzinc | 10 | 7 |
| 25 | " " | " | 20 | 9 |

EXAMPLES 26 AND 27.

The procedure described in Example 2 was repeated using 5% β -caryophyllene as the terpene and the remaining additives shown in Table III.

TABLE III

| Example | % Sulphur Compound | Zinc Compound | Parts/ Million as Zinc | Time of Onset of Colour (Minutes) |
|---------|---|--|------------------------------|--|
| 5 26 | 5% dodecanethiol | mercaptide of dodecanethiol | 20 | 9 |
| 27 | 5% disulphide of iso- octyl β -mercapto- propionate | mercaptide of iso- octyl β -mercapto- propionate | 20 | 10 |

EXAMPLES 28—30.

The procedure described in Example 2 was repeated using 5% nopadiene as the terpene and the remaining additives shown in Table IV.

TABLE IV

| Example | % Sulphur Compound | Zinc Compound | Parts/ Million as Zinc | Time of Onset of Colour (Minutes) |
|---------|------------------------------------|-------------------------------------|------------------------------|--|
| 28 | 5% dodecanethiol | mercaptide of dodecanethiol | 20 | 9 |
| 29 | 5% bis-t-butylphenyl disulphide | mercaptide of t- butylthiophenol | 20 | 8 |
| 30 | 5% 4-chlorobenzene- thiol. | dilaurylzinc | 20 | 10 |

EXAMPLES 31 AND 32.

The procedure described in Example 2 was repeated using 5% pinocarveol as the terpene and the remaining additives shown in Table V.

TABLE V

| Example | % Sulphur Compound | Zinc Compound | Parts/ Million as Zinc | Time of Onset of Colour (Minutes) |
|---------|---|--|------------------------------|--|
| 31 | 5% dodecanethiol | mercaptide of dodecanethiol | 20 | 8 |
| 32 | 5% bis- β -phenyl-ethane disulphide | mercaptide of β -phenylethanethiol | 20 | 9 |

EXAMPLE 33.

9 g. of powdered polyvinyl fluoride, 0.5 g. of β -pinene, 0.5 g. of dodecanethiol and 2.5 mg. of the zinc mercaptide of dodecanethiol were thoroughly mixed. A two gram sample of this mixture was pressed between nickel plates in a Carver press at 208° C. and 30 tons pressure for 10 minutes. The plates were cooled in water and the pressed film was removed. The film showed no evidence of colour when viewed against a white background.

A film made from the same composition but without the zinc mercaptide showed a yellow cast when viewed against a white background.

Films produced by the process of the present invention may be further subjected to orientation, heat setting and coating processes such as described in our Specifications Nos. 13431/60 and 37980/59 (899,830 and 901,746 respectively). These films are useful in a variety of commercial applications such, for example, as skin packages, heat-shrinkable wraps, window cartons, bundling material, egg and vegetable cartons, disposable throw-away containers, and packages of all types, protective covers for hats, shoes, hay stacks, farm equipment, car seats, mattresses, car licenses, drawing boards, furniture, appliances, window wells, ground covers, etc., painter's drop cloths, recording tapes, pressure-sensitive tapes, electrical tapes, metallized tapes, tear tapes, substrates for photographic and drafting purposes, typewriter ribbons, as a surfacing material, as a glazing material, in laminates with, for example, aluminium foil, decorative yarns, belting, webs, baskets, bases for ice rinks and pools, vapour barrier material, bee veils, dress shields, in neckwear and overshoe construction, in umbrellas, bathinettes and tents.

WHAT WE CLAIM IS:—

1. Compositions composed primarily of a halogen-containing hydrocarbon polymer with smaller amounts of at least one olefinically unsaturated terpene or an oxygen, halogen or hydrocarbon derivative of an olefinically unsaturated terpene, and of at least one thio

compound having the formula $R-S-H$ or $R-S-S-R^1$ where R and R^1 are the same or different and are alkyl, hydroxyalkyl, thioalkyl, carboalkoxyalkyl, carboxyalkyl, aralkyl, aryl, alkaryl, haloaryl, thioaryl, thioalkaryl, carboalkoxyaryl, carboxyaryl, cycloalkyl, or thienyl groups, and also containing a small amount of a finely dispersed (as herein before defined) organometallic compound of zinc having the formula R^{11}_2Zn wherein R^{11} is an aryl group or an alkyl group having 1–18 carbon atoms, or of a finely dispersed zinc derivative of a compound having at least one active hydrogen atom and an ionization constant of at least 1×10^{-16} , or of finely dispersed zinc or zinc oxide.

2. Compositions according to claim 1, in which the halogen-containing hydrocarbon polymer is polyvinyl chloride or polyvinyl fluoride.

3. Compositions according to claim 1 or 2, containing at least 1% of the terpene component, based on the weight of the additives plus polymer.

4. Compositions according to any one of the preceding claims, in which the terpene component is β -pinene, β -caryophyllene, pinocarveol or nopadiene.

5. Compositions according to any one of the preceding claims, containing at least 1% of the thio component, based on the weight of the additives plus polymer.

6. Compositions according to any one of the preceding claims, in which the thio component is decanethiol, dodecanethiol or octadecanethiol.

7. Compositions according to any one of the preceding claims, in which the total proportion of the terpene and thio components is 2–15%, based on the weight of the additives plus polymer.

8. Compositions according to any one of the preceding claims, in which the zinc compound is present in an amount 3–50 parts by weight of zinc per million parts by weight of polymer.

9. Compositions according to any one of

the preceding claims, in which the zinc compound is zinc laurate, dilaurylzinc, or the zinc mercaptide of isooctyl β -mercapto propionate or 1-dodecanethiol.

- 5 10. Halogen - containing hydrocarbon polymer compositions according to claim 1 substantially as hereinbefore described.

- 10 11. A process for forming shaped structures of halogen-containing hydrocarbon polymers, which comprises heating a composition claimed in any one of the preceding claims to convert it into a homogeneous single phase composition, forming the hot homogeneous single phase composition into a shaped structure, and cooling the shaped structure.

- 15 12. Process according to claim 11, in which

the shaped structure is formed by melt extrusion.

13. Process according to claim 11 or 12, in which the shaped structure is a self-supporting film. 20

14. A process for forming shaped structures according to claim 11 substantially as hereinbefore described.

15. Shaped structures of halogen-containing hydrocarbon polymers obtained by a process claimed in any one of claims 11 to 14. 25

J. A. KEMP & CO.,
Chartered Patent Agents,
14, South Square, Gray's Inn,
London, W.C.1.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1963. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.